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Selective Regeneration of Carbonyl Compounds from Oximes with N-Bromosuccinimide Under Neutral and Mild Conditions

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Summary. N-Bromosuccinimide has been found to be an efficient and selective reagent for the mild oxidative cleavage of oximes to yield their corresponding carbonyl compounds in good to excellent yields.

Keywords. Carbonyl compounds; Deoximation; N-bromosuccinimide; Oximes.

Selektive Regenerierung von Carbonylverbindungen aus Oximen mit N-Bromsuccinimid unter milden neutralen Bedingungen

Zusammenfassung. N-Bromsuccinimid ist ein effizientes und selektives Reagens zur milden oxidativen Spaltung von Oximen. Die entsprechenden Carbonylverbindungen werden in guten bis ausgezeichneten Ausbeuten erhalten.

Introduction

There has been considerable interest in the development of mild methods for the regeneration of carbonyl compounds from stable and readily prepared oximes and tosylhydrazones [1] due to the fact that such derivatives of carbonyl compounds serve as efficient protecting groups for aldehydes and ketones in organic synthesis [2]. Moreover, since oximes can be prepared from non-carbonyl compounds [3], the regenerated carbonyl compounds from oximes provide an alternative method for the preparation of aldehydes and ketones. Most of the known methods of regenerating carbonyl compounds from their nitrogen derivatives require strongly acidic [4], oxidative [5], or reductive [6] conditions. Recently, clay supported ferric nitrate [7], dimethyl dioxirane [8], pyridinium dichromate-*t*-butyl hydroperoxide [9], iodosobenzene diacetate [10], the titanium silicalite-1-H_2O_2 combination [11], and 70% *TBHP* [12] have been reported to cleave the C=N bond of oximes and tosylhydrazones. However, many of the conventional procedures for regeneration

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of the carbonyl function from such nitrogen derivatives have several limitations: some of the reagents are hazardous or very toxic, expensive, or not readily available, or they need to be freshly prepared and the reactions require drastic conditions, long reaction times, and tedious work-up. It is important that most of the reported methods are suitable for the regeneration of ketones from their oximes and tosylhydrazones and not for aldehydes where the yields are low due to the overoxidation of regenerated aldehydes to acids. Therefore, it is desirable that a method which involves relatively mild reaction conditions should be available, leading to high recoveries of a wide range of aldehydes and ketones. We now report an efficient and general method for the effective and selective cleavage of oximes with N-Bromosuccinimide (*NBS*) under neutral and mild conditions.

Results and Discussion

Dissolution of oximes in acetone with addition of a small amount of water and subsequent reaction with *NBS* under stirring at room temperature (25°C) or reflux gave the corresponding carbonyl compounds in good yields. Table 1 summarizes the results of various oximes which underwent oxidative cleavage with *NBS* to form the corresponding carbonyl compounds. The rate of oxidative cleavage of 4-bromobenzophenone oxime was fast. Even the sterically hindered ketone oximes (entries 12–13) were successfully oxidatively cleaved to the corresponding ketones in good yields. The unsaturated cinnamaldoxime (entry 2), however, was first brominated at the C=C double bond followed by deoximation. The most remarkable advantage of this methodology is that it is a general method for oxidative cleavege of a variety of aldoximes and ketone oximes with *NBS* under neutral and mild conditions, and no trace of acid was formed due to overoxidation of the regenerated aldehyde.

This procedure is also useful for the chemoselective oxidative deoximation of ketone oximes in the presence of aldoximes. Thus, when equimolar mixtures of 3-nitrobenzaldoxime and cyclopentanone oxime, 2-nitrobenzaldoxime and acetophenone oxime, or salicylaldoxime and 4-bromobenzophenone oxime in acetone and water were allowed to react with *NBS* as room temperatures (25°C) for a period of 2.5 h, 3.2 h, and 0.5 h, respectively, the ketone oximes cyclopentanone oxime, acetophenone oxime, and 4-bromobenzophenone oxime underwent chemoselctively oxidative deoximation giving 65% cyclopentanone, 71% acetophenone, and 85% 4-bromobenzophenone, whereas the aldoximes 3-nitrobenzaldoxime, 2-nitrobenzaldoxime, and salicylaldoxime were recovered unchanged.

In conclusion, we hope that the presented deprotection and deoximation methodology of oximes will find wide application in organic synthesis because of the simplicity of work-up and the use of readily available oxidant *NBS* under neutral and mild conditions.

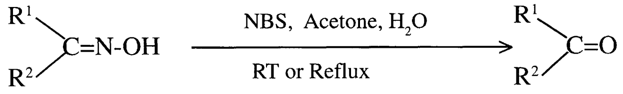
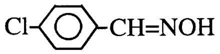
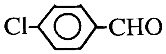
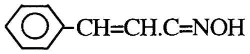
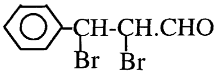
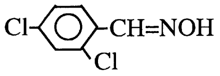
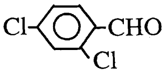
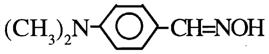
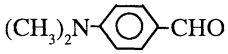
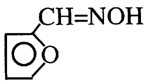
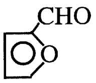
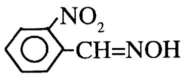
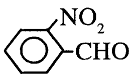
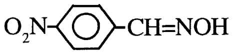
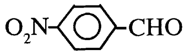
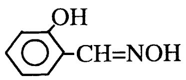
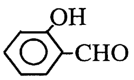
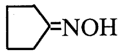
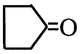
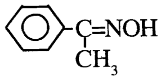
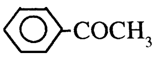
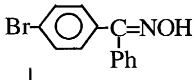
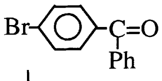
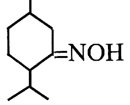
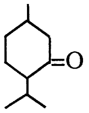
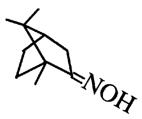
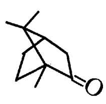


Table 1. Oxidative cleavage of oximes with *NBS*

Entry	Substrate	Reaction conditions		Product	Yield[a](%)
		Temp. (°C)	Time (h)		
1		60	1		95
2		25	5		70[b]
3		25	2.5		65
4		25	5		88
5		25	3.5		60
6		60	5		85
7		25	1.2		88
8		25	4.3		48
9		25	2.5		67
10		25	3.2		75
11		25	0.5		86
12		25	1.5		87
13		25	1.5		84

[a] isolated yields; [b] requires 4 equivalents of *NBS*

Experimental

General procedure

A mixture of the oxime (3 mmol) and *NBS* (3.1 mmol) in acetone (10 ml) and water (1 ml) was stirred at the temperature given in Table 1 for the specified time. After the reaction was complete (TLC), the solvent was removed under reduced pressure, and the product was purified by column chromatography. Products were characterized by IR and ^1H NMR spectroscopy as well as by comparison with authentic samples.

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